higher value than unity, and this was found experimentally.

The polymerization product from maltose is similar to polyglucose. The hydrolysis product was D-glucose, and the physical characteristics of the polymer were similar to that of a polyglucose produced by a low temperature short polymerization cycle. The lower amount of periodate consumption and formic acid production of the polymer from maltose, as compared to that of a polyglucose produced at higher temperature and upon longer heating,[2,5] indicate, however, that the polymer of maltose is more branched than polyglucose. The somewhat higher restriction of initial mobility of the dimer during the melt polymerization might account for this phenomenon. In any case, rearrangement of the polysaccharide linkage and randomization with respect to sequence of linkages, and establishment of $\alpha$-$\beta$ and pyranose-furanose equilibrium are expected to give a product essentially similar to that of polyglucose.[1-3,13]

The polymers of aldoses are apparently all highly branched, the aldohexose polymers being more branched than the aldopentose polymers because of the higher functionality of the monomer.[14]

The different linkages are expected to be distributed randomly in all the polysaccharides, since there is no reason for them to be otherwise in a chemically catalyzed polymerization. Also, since the reactivities of the functional groups are more alike at high temperature, their simultaneous availability for condensation should lead to more branching, and if the activating energy is high enough to cause condensation at each hydroxyl, eventually all possible linkages are to be expected. However, structural (methylation) studies should be carried out to substantiate this and other arguments presented above. It is further assumed that the amount of the $\alpha$- and $\beta$-glycosidic links, and the furanose and pyranose rings, correspond to the equilibrium concentration established during the polymerization.[2,3]

The above experiments are described in order to illustrate the general utility of our polycondensation method for aldoses. By this method a large number of new synthetic polysaccharides became available for structural and biological investigations. Results of such investigations will be reported in due course, as well as further polymerization experiments with restricted functional groups on monomers leading to different polymers.

(14) *Cf.* P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter IX, pp. 347-398.

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[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA]

# Methylation Studies on Dialdehydes Obtained from Methyl Glycosides by Periodate Oxidation[1]

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RECEIVED OCTOBER 12, 1959

Evidence is presented to support the view that the so-called "dialdehydes" produced by the periodate oxidation of methyl glycosides exist in the cyclic form as derivatives of dioxane.

In previous communications[2-4] it was shown that the so-called dialdehydes formed by periodate oxidation of methyl glycosides exist in the cyclic acetal form as derivatives of dioxane. This conclusion was reached from infrared and polarimetric measurements and also because the "dialdehydes" reacted not as carbonyl but as hydroxy compounds. Thus the so-called dialdehyde formed by periodate oxidation of methyl $\alpha$-L-rhamnopyranoside gave rise to a crystalline di-*p*-nitrobenzoate, and methylation with silver oxide and methyl iodide furnished a dimethyl ether.

This paper is concerned with methylation studies on three additional "dialdehydes" (I, IV and VII) which further support the view that these substances exist in the cyclic form as derivatives of dioxane.

The "dialdehyde" I, prepared from methyl $\beta$-L-arabinopyranoside by periodate oxidation, gave upon treatment with silver oxide and methyl iodide a sirupy product, 2(D″), 3,5-trimethoxy-1,4-dioxane (III),[5] the methoxyl content of which indicated that two methoxyl groups had been introduced during methylation. Furthermore, the rotation ($[\alpha]^{24}D$ +124° in ethanol) of III was comparable with that of the starting material which showed $[\alpha]^{20}D$ +125° in water. This similarity in rotation suggested[3] that the oxidation product I possessed the cyclic structure II.

The compound D′-methoxy-D-methoxymethyl-diglycolic aldehyde (IV) obtained by periodate oxidation of methyl 6-*O*-methyl-$\alpha$-D-galactopyranoside also reacted in the cyclic form (V) because upon methylation with silver oxide and methyl iodide 2(D″),3,5-trimethoxy-6(L″)-methoxymethyl-1,4-dioxane (VI)[5] was formed. The compound VI which showed $[\alpha]^{22}D$ +150° (in ethanol) as compared with $[\alpha]^{21}D$ +143° (in ethanol) for the starting

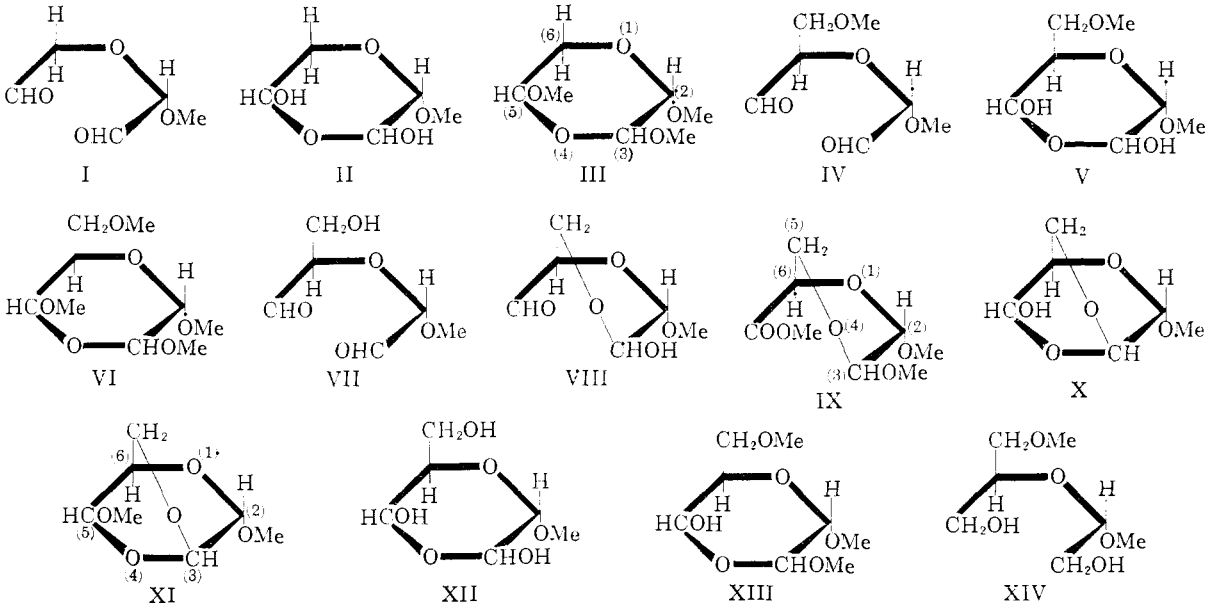
(1) Paper No. 4215 Scientific Journal Series, Minnesota Agricultural Experiment Station, University of Minnesota, St. Paul 1, Minn. This work was sponsored by the Office of Ordnance Research, U. S. Army.

(2) J. E. Cadotte, G. G. S. Dutton, I. J. Goldstein, B. A. Lewis, F. Smith and J. W. Van Cleve, THIS JOURNAL, **79**, 691 (1957).

(3) I. J. Goldstein, B. A. Lewis and F. Smith, *ibid.*, **80**, 939 (1958).

(4) I. J. Goldstein, B. A. Lewis and F. Smith, *Chemistry & Industry*, 595 (1958).

(5) Groups designated by D″ and L″ in this and other formulations of dioxane compounds correspond to positions below and above the plane of the ring of the original formula written according to the Haworth convention (*cf.* ref. 3).




product IV, contained four methoxyl groups showing that two of them were introduced during the methylation reaction. Consequently the so-called "dialdehyde" IV is represented as the 1,4-dioxane derivative V.

There is only one way in which the two "dialdehydes" I and IV cited above can undergo cyclization and this involves the sharing of a molecule of water between the two aldehydic groups at $C_2$ and $C_4$ of the original glycoside.[2-4] Inspection of the structure for the "dialdehyde" VII formed upon periodate oxidation of methyl $\alpha$-D-glucopyranoside shows that this substance can exist in a number of isomeric modifications, because, discounting the isomerization at any newly formed asymmetric center, three structurally different isomers VIII, X and XII may be formed.[6] The first of these, VIII, has been postulated previously[2,7] on the evidence that mild catalytic reduction in the presence of a palladium–charcoal catalyst effected preferential reduction at $C_4$ leaving the aldehydic group at $C_2$ intact.

Evidence that this type of isomerization of VII is possible is shown by the fact that when VII ($[\alpha]^{20}D$ +121° in water) was treated with silver oxide and methyl iodide a vigorous reaction ensued and a mixture of two crystalline products, believed to be IX and XI, was formed.

Compound IX, 2(D″), 3-dimethoxy-6(D″)-carbomethoxy-1,4-dioxane,[8] was readily separated from compound XI because it was more soluble in methanol. Elementary analysis, a determination of the methoxyl content, saponification equivalent and the preparation of a crystalline amide served to characterize IX. Furthermore, the high rotation ($[\alpha]^{25}D$ +183° in chloroform) was indicative[3] of the presence of a ring system. Infrared analysis showed the presence of a carbonyl group which could be interpreted to be an ester grouping, but no hydroxyl group was detected. The configuration at positions 2 and 6 (of the 1,4-dioxane compound IX) is believed to be the same as that in the original glycoside; however that at position 3 can be either D or L or a D,L mixture of the anomeric forms and in the absence of any diagnostic evidence IX was designated as a D,L-mixture with respect to position 3 of the 1,4-dioxane compound. It will be apparent that this compound is the methylated analog of the cyclized dialdehyde VIII in which the aldehydic group at $C_4$ of the original glycoside has been oxidized and transformed into the corresponding methyl ester, a reaction that is not unexpected, inasmuch as the oxidizing action of silver oxide in the presence of methyl and ethyl iodide is well known.[9]

The methanol-insoluble crystalline product XI is believed to be 2 (D″), 5-dimethoxy-(3,6-L″-oxymethylene)-1,4-dioxane. The experimental evidence in support of structure XI is: The compound XI was unaffected by treatment with alkali, it resisted reduction with sodium borohydride and it did not react with neutral or alkaline permanganate. Infrared analysis showed that hydroxyl and carbonyl groups were absent whereas the presence of methoxyl groups was readily recognized. Upon methanolysis XI gave rise to D-glyceraldehyde dimethylacetal recognized as its crystalline di-*p*-nitrobenzoate.

Consideration of the structure of XI shows that this compound may exist in four stereoisomeric forms, because two asymmetric centers at position 3 and position 5 are introduced by the cyclization. However the bridgehead between position 3 and position 6 can be introduced in only one manner inasmuch as there is only one configuration for the group at position 6 and consequently there is good reason to believe that XI exists in no more than two diastereoisomeric forms as a result of dis-

(6) C. D. Hurd, P. J. Baker, R. P. Holysz and W. H. Saunders, *J. Org. Chem.*, **18**, 186 (1953).

(7) B. A. Lewis, R. Montgomery, F. Smith and J. W. Van Cleve, 121st A.C.S. Meeting, Milwaukee, Wis., March, 1952.

(8) I. J. Goldstein and F. Smith, THIS JOURNAL, **80**, 4681 (1958).

(9) J. C. Irvine, J. L. A. Macdonald and C. W. Soutar, *J. Chem. Soc.* **107**, 337 (1915).

symetery at position 5. The rather high positive rotation ($[\alpha]^{25}D$ +152° in chloroform) of XI lends support to its representation as the methylated analog of X. The fact that XI is crystalline indicates that it assumes one of the two possible configurations, but it is not yet possible to decide between the two.

A liquid product remaining after the isolation of IX and XI reacted in a manner that was consistent with the presence of isomers of IX (isomerization at position 3) and XI (isomerization at position 5). Thus treatment of the liquid product with methanolic hydrogen chloride afforded methyl glycerate the latter arising from IX or its isomer. Sodium borohydride reduction of the methanolyzate yielded glyceritol which was most probably derived from the methyl glycerate from IX or its isomer and not from the glyceraldehyde dimethylacetal that would be derived from XI or its isomer; the trace amounts of methyl glycerate detected may have been obtained from material that did not undergo reduction. Acid hydrolysis of the methanolyzate of the liquid fraction followed by reduction with sodium borohydride gave glyceritol, the product to be expected from the glyceraldehyde component derivable from XI or its isomer and not from the glyceric acid from IX or its isomer. Direct reduction of the liquid fraction with sodium borohydride followed by acid hydrolysis gave rise to glyceritol (by reduction of the –COOMe group of IX or its isomer) and methyl glycerate (incomplete reduction of the –COOMe group) both of which arise from IX or its isomer and not from XI. Trace amounts of 1-*O*-methylglyceritol were found in hydrolyzates of the liquid fraction after methanolysis and reduction or after reduction and hydrolysis; the exact mechanism of the formation of 1-*O*-methylglyceritol is not known but it is believed that steric hinderance might lead to incomplete methylation of XII at position 5 giving XIII. The latter is not stable[9] and reduction of it would afford XIV which upon hydrolysis would yield 1-*O*-methylglyceritol. Similarly, hydrolysis preceding reduction with borohydride would also be expected to yield 1-*O*-methylglyceritol. In support of this hypothesis it was found that the 1-*O*-methylglyceritol was not generated directly from the liquid fraction by hydrolysis but only after reduction had been applied.

These methylation studies lend further support to the contention that the products obtained upon periodate oxidation of glycosides[1-3,5] and of polysaccharides[8,10] possess cyclic acetal structures.

## Experimental

(1) **Methylation of D'-Methoxy-D-methoxymethyl Diglycolic Aldehyde with Methyl Iodide and Silver Oxide.**—To a solution of D'-methoxy-D-methoxymethyldiglycolic aldehyde (172 mg.), prepared by periodate oxidation of methyl 6-*O*-methyl-α-D-galactopyranoside,[11] in methyl iodide (20 ml.), was added silver oxide (0.5 g.). After 5 min. the clear reaction mixture became cloudy, then very turbid, although no heat was liberated. After standing 1 hr. at room temp. the reaction mixture was boiled under reflux for 15 hr., silver oxide (0.25 g.) being added every 3 hr.

Extraction with ether and evaporation of the solvent gave a mobile, water-insoluble, yellow liquid (183 mg.). This liquid did not contain an ester grouping (tested by heating with 0.05 *N* sodium hydroxide in the presence of phenolphthalein). Distillation gave 2(D'), 3,5-trimethoxy-6-(L")-methoxymethyl-1,4-dioxane (VI) as a colorless liquid (160 mg.), b.p. (bath temp.) 130–140° (3 mm.), $n^{23}D$ 1.4365 and $[\alpha]^{22}D$ +150° in ethanol (*c* 1).

*Anal.* Calcd. for $C_9H_{18}O_6$: C, 48.64; H, 8.16; $OCH_3$, 55.8. Found: C, 48.44; H, 9.13; $OCH_3$, 54.0.

After two additional treatments with methyl iodide and silver oxide, the product was dissolved in 50% ethanol (5 ml.) to which was added an anion exchange resin (1 g. of Amberlite IR4A).[12] The mixture was boiled under reflux in order to hydrolyze any ester and absorb the anion so formed. The resin was filtered and the filtrate concentrated to a yellow sirup (118 mg.) which distilled as a mobile, colorless liquid (100 mg.), b.p. 135° (3 mm.) (bath temp.), $n^{21}D$ 1.4378, $[\alpha]^{22}D$ + 151° in ethanol (*c* 1.1).

*Anal.* Calcd. for $C_9H_{18}O_6$: $OCH_3$, 55.8. Found: $OCH_3$, 54.0.

(2) **Methylation of D'-Methoxydiglycolic Aldehyde with Silver Oxide and Methyl Iodide.**—To a solution of D'-methoxydiglycolic aldehyde (850 mg.) (prepared in the usual manner[13,14] from methyl β-L-arabinopyranoside by periodate oxidation) in methyl iodide (20 ml.), silver oxide (1 g.) was added. The reaction solution which became cloudy after 40 min. was allowed to stand at room temp. for an additional 4 hr. and then refluxed for 20 hr. The product was isolated as described above and subjected to two further treatments with silver oxide and methyl iodide. The product so formed, a pale yellow mobile liquid (0.663 g.) having $[\alpha]^{24}D$ +122° in ethanol (*c* 1.5), was dissolved in 0.1 *N* potassium hydroxide (50 ml. of a 50% aqueous ethanolic solution). Heating at 50° for 1 hr. caused a slight change in rotation ($\alpha^{29}D$ +1.60° → +1.57°, constant, 1-dm. tube). The ethanol was distilled and the residue dissolved in chloroform (25 ml.). The chloroform extract was washed with water (3 × 20 ml.), dried, and concentrated to give a mobile yellow sirup (0.565 g.) which upon distillation gave 2(D"),3,5-trimethoxy-1,4-dioxane (III), a colorless, mobile liquid (275 mg.), b.p. (bath temp.) 145–150° (10 mm.), $n^{24}D$ 1.4305, $[\alpha]^{24}D$ +124° in ethanol (*c* 1).

*Anal.* Calcd. for $C_7H_{14}O_6$: $OCH_3$, 52.2. Found: $OCH_3$, 50.3.

(3) **Methylation of D'-Methoxy-D-hydroxymethyldiglycolic Aldehyde (VII) with Methyl Iodide and Silver Oxide.**—Silver oxide (6 g.) was added to a cooled mixture of the dialdehyde VII (4.265 g., obtained from the periodate oxidation of methyl α-D-glucopyranoside) and methyl iodide (25 ml.). A vigorous reaction ensued upon slowly warming the reaction mixture to room temperature. The reaction was moderated by cooling in an ice-bath and after standing in a refrigerator overnight the reaction mixture, which had become homogeneous, was refluxed for 5.5 hr. with frequent shaking. Distillation of methyl iodide followed by extraction with chloroform and with ethanol and concentration of the combined extracts gave a yellow sirup which underwent partial crystallization. The product, now completely soluble in methyl iodide, was submitted to four additional methylations with methyl iodide (20 ml.) and silver oxide (3 g.), the reaction mixture being refluxed each time and isolated by extraction with chloroform.

The product (3.95 g.) so obtained was dissolved in ethanol (20 ml.). Upon cooling, spontaneous crystallization occurred. Filtration yielded a white crystalline powder (730 mg.) which showed $[\alpha]^{25}D$ +165° in chloroform (*c* 0.9). The product was a mixture, part of it melting at 120–121° and the rest at 245–250°. Resolution of the material into two pure crystalline compounds was effected by dissolving the lower melting component, constituting the major proportion of the product, in warm methanol (about 20 ml.). The methanol-insoluble portion which remained was recrystallized from a large volume of ethanol to yield 2(D''),5-dimethoxy-(3,6-L''-oxymethylene)-1,4-dioxane (XI) as white needles (50 mg.), m.p. 252° which sublimed unchanged,

(10) I. J. Goldstein and F. Smith, *Chemistry & Industry*, 40 (1958); M. Abdel-Akher and F. Smith, THIS JOURNAL, **81**, 1718 (1959).

(11) I. J. Goldstein, J. K. Hamilton and F. Smith, *ibid.*, **79**, 1190 (1957).

(12) A product of the Rohm and Haas Chemical Co., Philadelphia, Pa.

(13) E. L. Jackson and C. S. Hudson, THIS JOURNAL, **58**, 378 (1936); **59**, 994 (1937).

(14) J. W. Van Cleve and F. Smith, *ibid.*, **77**, 3091 (1955).

$[\alpha]^{25}D$ +152° in chloroform (*c* 0.7). *Anal.* Calcd. for $C_7H_{12}O_5$: C, 47.6; H, 6.83; $OCH_3$, 35.2. Found: C, 47.9; H, 7.1; $OCH_3$, 35.6.

The methanolic filtrate left after isolating XI was concentrated *in vacuo* to a white solid which was recrystallized twice from ethanol to give fine white needles (480 mg.) of 2(D'')3-dimethoxy-6-(D'')-carbomethoxy-1,4-dioxane (IX), m.p. 124–126°, $[\alpha]^{25}D$ +183° in chloroform (*c* 1).

After removing the crystalline product consisting of a mixture of compounds IX and XI, the filtrate was concentrated to a pale yellow sirup (3.1 g.) which was distilled giving: fraction 1 (1.580 g.), b.p. (bath temp.) 122–128° (3 mm.), $n^{26}D$ 1.4385; fraction 2 (0.330 g.), b.p. (bath temp.) 160–175° (0.02 mm.), $n^{26}D$ 1.4670; fraction 3 (0.627 g.), b.p. (bath temp.) 185–200° (0.02 mm.), $n^{26}D$ 1.4655.

Fraction 1 crystallized spontaneously. Recrystallization from ethanol gave IX (100 mg.), m.p. 125–127°, $[\alpha]^{25}D$ +180° in chloroform (*c* 0.5). The product from the mother liquors was redistilled to give: fraction 1a, 1.117 g. (colorless liquid), b.p. (bath temp.) 120° (3 mm.), $n^{23}D$ 1.4390, $[\alpha]^{26}D$ +130° in ethanol (*c* 1). Found: OMe[15] 40.6; fraction 1b, 0.205 g., b.p. (bath temp.) 120–130° (3 mm.), $n^{23}D$ 1.4410. Found: OMe,[15] 40.0.

**Identification of 2(D'')3-Dimethoxy-6(D'')-carbomethoxy-1,4-dioxane (IX).**—The substance IX obtained as fine white needles having m.p. 124–126°, $[\alpha]^{25}D$ +183° in chloroform (*c* 1) was soluble in methanol, ethanol, chloroform and acetone but insoluble in water; IX did not reduce Fehling solution but it contained an ester grouping as revealed by a fading of the pink coloration of phenolphthalein when it was heated in the presence of dilute alkali (0.05 *N*) (ingress of atmospheric $CO_2$ prevented). Infrared analysis of IX revealed the presence of =CO and —$OCH_3$ but no —OH groups.

*Anal.* Calcd. for $C_8H_{14}O_6$: C, 46.6; H, 6.8; $OCH_3$, 45.1; sapon. value, 206. Found: C, 46.9; H, 7.0; $OCH_3$, 45.3; sapon. value, 212.

Reduction of IX (15 mg.) with sodium borohydride followed by hydrolysis with *N* sulfuric acid at 95° for 6 hr. gave glyceritol as detected by paper chromatography.

Treatment of the ester IX with methanolic ammonia for 1 day followed by removal of solvent gave a small amount (3 mg.) of XI, m.p. 252° (after recrystallization from ethanol). The mother liquor was concentrated, dissolved in methanol (15 ml.) and retreated with gaseous ammonia as above. The reaction mixture was permitted to stand at room temperature for 15 hr. Evaporation of the methanol gave a crystalline residue which after two recrystallizations from petroleum ether–ethanol gave 2(D'')3-dimethoxy-6-(D'')-carboxamide-1,4-dioxane in the form of fine white needles, m.p. 98°, $[\alpha]^{26}D$ +227° in chloroform (*c* 0.8). Microscopic examination showed that tiny white granules (XI ?) were adhering to the needles thus indicating that the substance was not quite pure, a view supported by the analysis.

*Anal.* Calcd. for $C_7H_{13}O_5N$: C, 44.0; H, 6.85; N, 7.32; $OCH_3$, 32.5. Found: C, 44.56; H, 6.90; N, 7.00; $OCH_3$, 33.2.

**Identification of 2(D'')5-Dimethoxy-(3,6-L''-oxymethylene)-1,4-dioxane (XI).**—This inert compound apparently occurs in two crystalline forms, fine white needles and feathery white needles, both showing m.p. 252° and subliming without decomposition.

The white needles, which showed $[\alpha]^{25}D$ +152° in chloroform (*c* 0.66), were soluble in chloroform, and 1,4-dioxane but insoluble in ethanol, methanol and in water. The product did not reduce Fehling solution and it gave a negative ester test. The substance XI was not affected by alkali, neutral or alkaline potassium permanganate solution, or by sodium borohydride (tested in methanol–1,4-dioxane (1:3)). Infrared analysis of XI revealed the presence of —$OCH_3$ but neither =CO nor—OH groups could be detected.

A suspension of XI (0.011 g.) in methanol (1 ml.) containing 5% hydrogen chloride was heated (sealed tube) in a boiling water-bath for 2.5 hr. The reaction mixture was cooled to 5°, the tube opened, and the solution neutralized ($Ag_2CO_3$). Filtration and evaporation gave a sirup which was found by paper chromatography (solvent, butanone–water azeotrope; spray reagent, ammoniacal $AgNO_3$) to contain glyceraldehyde dimethylacetal ($R_f$ 0.53).

The glyceraldehyde dimethylacetal was separated from a slower moving component by sheet paper chromatography using butanone–water azeotrope. Extraction of the appropriate area of the paper with water followed by evaporation of the solvent yielded pure glyceraldehyde dimethylacetal which was dissolved in pyridine (0.5 ml.) and heated with *p*-nitrobenzoyl chloride (0.05 g.) for 0.5 hr. at 85°. The reaction mixture was cooled and treated with an excess of a saturated aqueous solution of sodium bicarbonate. The precipitate thus formed was separated (centrifuge) and washed successively with aqueous sodium bicarbonate, water, and with ethanol. After being dried *in vacuo* the product was dissolved in chloroform (3 ml.), treated with charcoal and filtered. Evaporation of the solvent almost to dryness and addition of a drop of ethanol caused crystallization. After washing with ethanol and recrystallization from acetone–ethanol the D-glyceraldehyde dimethylacetal di-*p*-nitrobenzoate had m.p. and mixed m.p. 112°, $[\alpha]^{25}D$ +50° in chloroform (*c* 0.3). An authentic specimen of D-glyceraldehyde dimethylacetal di-*p*-nitrobenzoate had m.p. 112–113°, $[\alpha]^{25}D$ +53° in chloroform (*c* 1). *Anal.* Calcd. for $C_{19}H_{18}O_{10}N_2$: C, 52.54; H, 4.18; N, 6.45. Found: C, 52.8; H, 4.10; N, 6.28.

**Examination of Fraction 1a.**—Fraction 1a gave a negative Fehling test and a positive ester test. A solution of fraction 1a (160 mg.) in 7.7% methanolic hydrogen chloride (3 ml.) was heated (sealed tube) for 14 hr. at 135°. The slightly acid solution was neutralized with silver carbonate, filtered, and concentrated at atmospheric pressure to a yellow sirup which was purified by extraction with ether. The product was optically inactive. Paper chromatography using butanone–water azeotrope as the irrigating solvent and Tollens spray reagent showed the presence of a component having the same mobility as methyl glycerate ($R_f$ 0.61). No 1-*O*-methylglyceritol ($R_f$ 0.52) was detected.

Concentrated sulfuric acid (0.1 ml.) was added to a solution of one-half of the product obtained from methanolysis of fraction 1a in 40% aqueous ethanol (5 ml.) and the reaction mixture refluxed for 5 hr. Neutralization ($BaCO_3$), filtration and concentration of the filtrate *in vacuo* gave a yellow sirup which was dissolved in methanol (2 ml.). Sodium borohydride (50 mg.) was added. After 3 hr. the reaction mixture was acidified with acetic acid, concentrated and the residue extracted with acetone. The product contained glyceritol as revealed by paper chromatography thus indicating the presence of a glyceraldehyde residue in the original compound (fraction 1a).

The remainder of the product obtained from the methanolysis of fraction 1a was dissolved in methanol (5 ml.). Sodium borohydride (100 mg.) was added and the reaction mixture kept overnight. Acidification with acetic acid, concentration and analysis of the reaction mixture by paper chromatography using butanone–water azeotrope as irrigating solvent, showed upon spraying with Tollens reagent an intense spot for glyceritol ($R_f$ 0.19) as well as traces of 1-*O*-methylglyceritol ($R_f$ 0.58), methyl glycerate ($R_f$ 0.65) and an unknown component ($R_f$ 0.46).

**Examination of Fraction 1b.**—Sodium borohydride (50 mg.) was added to a solution of fraction 1b (52 mg.) in methanol (2 ml.). After 2 hr., 7% methanolic hydrogen chloride (4 ml.) was added (sodium chloride precipitated) and the mixture heated for 16 hr. at 135° in a Carius tube. The reaction mixture was filtered and concentrated *in vacuo* to distil any methyl borate. Neutralization with silver carbonate, filtration, and concentration *in vacuo* gave a yellow sirup. Paper chromatography using butanone–water azeotrope revealed that the product contained glyceritol ($R_f$ 0.17, major component), 1-O-methylglyceritol ($R_f$ 0.54, trace amount) and an unknown component ($R_f$ 0.43, moderate amount) which was identical with the component obtained when the methanolysis products of fraction 1a were reduced with sodium borohydride.

**Acknowledgment.**—The authors thank Dr. S. Fenton, Department of Organic Chemistry, University of Minnesota, for the infrared analyses.

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(15) G. Gran, *Svensk Papperstidn.*, **57**, 702 (1954).